Photoelectron Spectroscopy (PES) Worksheet

The following are links that give overviews about PES:

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Photoelectron_Spectroscopy/Photoelectron_Spectroscopy%3a_Application

http://chemwiki.ucdavis.edu/Physical_Chemistry/Spectroscopy/Photoelectron_Spectroscopy/Photoelectron_Spectroscopy%3A_Theory

http://www.youtube.com/watch?v=vANbxozsRSA

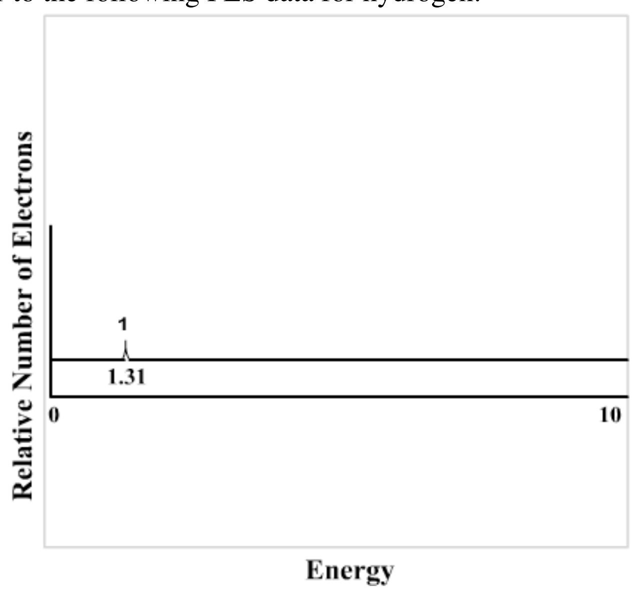
Photoelectron spectroscopy (PES) is a technique that is used to gather information about the electrons in an atom. In PES, an atom is bombarded with photons. Some of the photons are absorbed and electrons are emitted. The electrons are collected and their energy is analyzed. During PES, we know the energy of the photons we excite the electrons with. Since energy is conserved, the difference in the energy between the photons sent into the atom and the energy of the emitted electrons will be the potential energy of the electrons when they are attached to the atom. This is the Ionization Energy (IE) Remember that the potential energy of the electron in the atom is the work needed to remove the electron from the atom.

$$IE = E_{photon} - E_{emitted\ e}$$

The following URL has PES graphs for several elements:

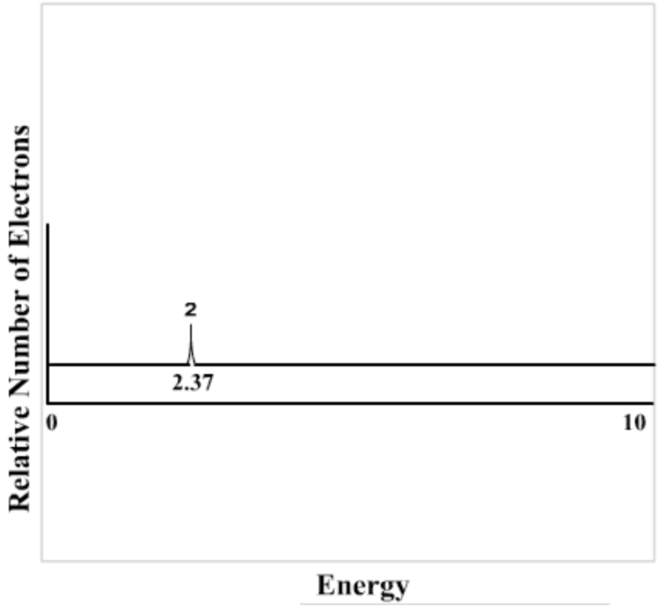
http://www.chem.arizona.edu/chemt/Flash/photoelectron.html

For the following questions refer to the following PES data for hydrogen:



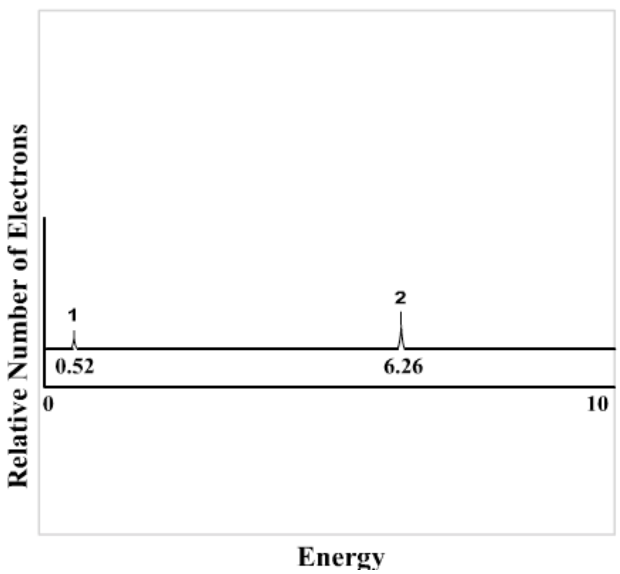
The peak on the graph has two numbers. The whole number on the top of the peak is the number of electrons the element has. The decimal number is the Ionization E needed to remove the electron from the atom in MJ/mol.

Now for the PES for helium:



You'll see that the number of electrons is 2 and the IE is higher than hydrogen. That's because He has 2 electrons and H has 1. Also, H and He have the same level of shielding (none) while He has 2 protons and H has 1. So the higher nuclear charge has a stronger attraction for the electrons, meaning that it takes more energy to remove the electrons from He than from H.

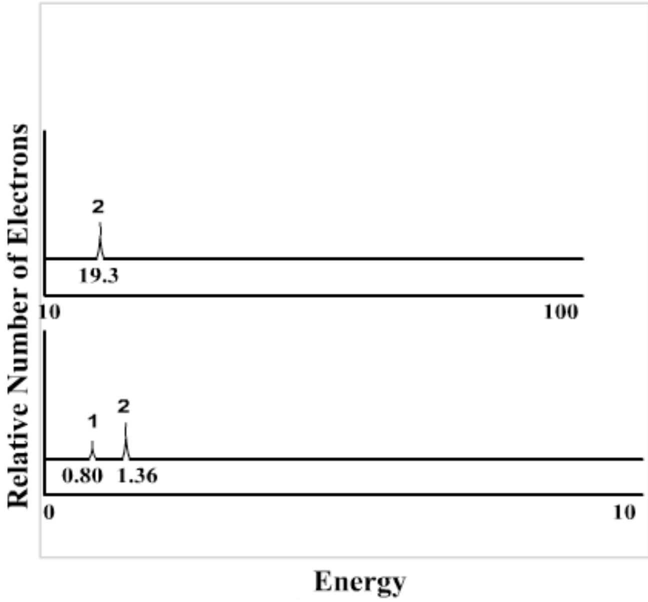
For lithium, there two sets of electrons in different energy levels.



In Li's spectrum above, there are two peaks. Of the two peaks, one is for the electron at the higher energy 2*s* level, and the other is for the two electrons in the lower energy 1*s* level. Let's think about terminology. We have said that electrons in 1s have lower potential energy than 2s. When we look at the PES spectrum, we see 1 electron at a low number, and 2 electrons at a high number. How can this be if the 2 electrons in 1s have lower energy than the 1 electron is 2s?

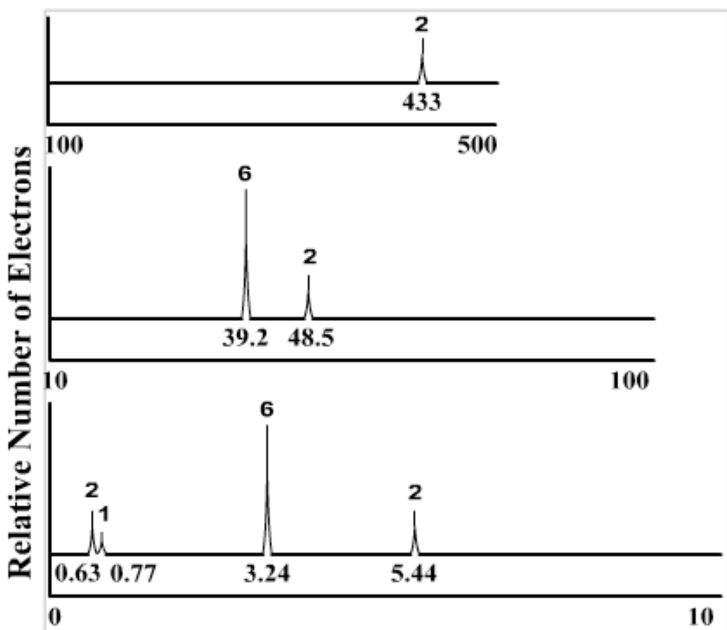
On the PES spectra, a high-energy number means the electron is closer to the nucleus and experiences more nuclear charge attraction, so more energy is needed to remove the electron. A low number means it is farther from the nucleus, experiences less nuclear charge attraction, so less energy is needed to remove it. Note that the peak for an electron farther from the nucleus is closer to the beginning of the graph while the peak for an electron closer to the nucleus is farther from the beginning of the graph.

Now look at boron's spectrum:



The two electrons at 19.3 MJ are the 1*s* electrons. There are also two electrons at 1.36 MJ and one electron at 0.80 MJ. The two electrons are 2*s* and the one electron is 2*p*. Why are they different? They are both in the same energy level (shell), so why do they have different potential energies? The reason the 2*s* and 2*p* orbitals have different energies is that *s* penetrates better than *p*. An *s* orbital can overcome the effect of shielding better than *p*, so more E is required to remove that 1*s* electron.

Looking at the spectrum for scandium:



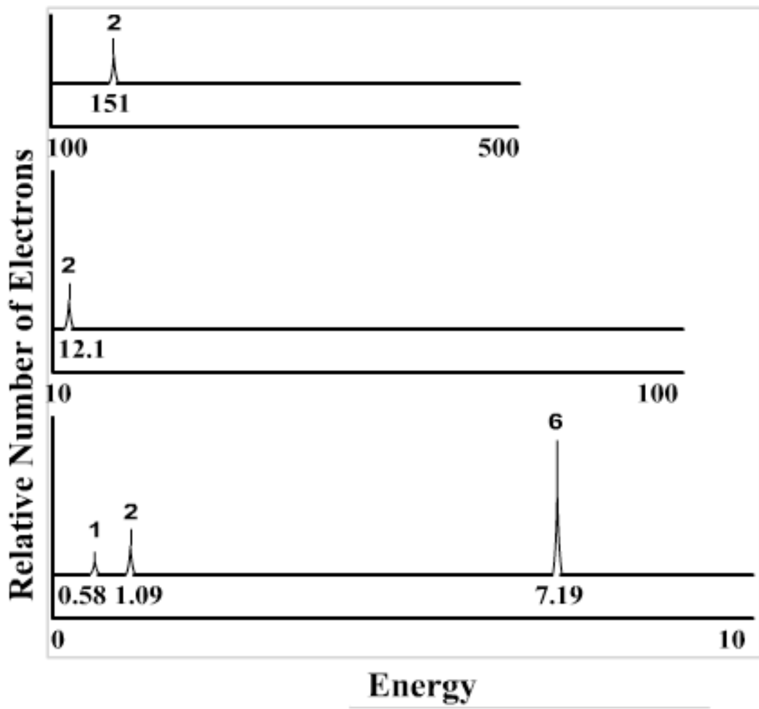
The filling order has 3*d* after 4*s* because 3*d* does not penetrate as well as 4*s*. However, in the spectrum for scandium we can see that there are two electrons at 0.63 MJ and one at 0.77 MJ. This suggests that it is easier to remove the 4*s* than the 3*d*. This is because the third energy level electrons shield electrons in the fourth energy level, so less energy is required to remove the 4*s* electrons.

Questions

1. What determines the position and the height (intensity) of each peak in a photoelectron spectrum?

2. Why is the distance of the energy level from the nucleus important in determining the corresponding peak position in the photoelectron spectrum?

3. a. The spectrum below is for which element? Explain your reasoning.

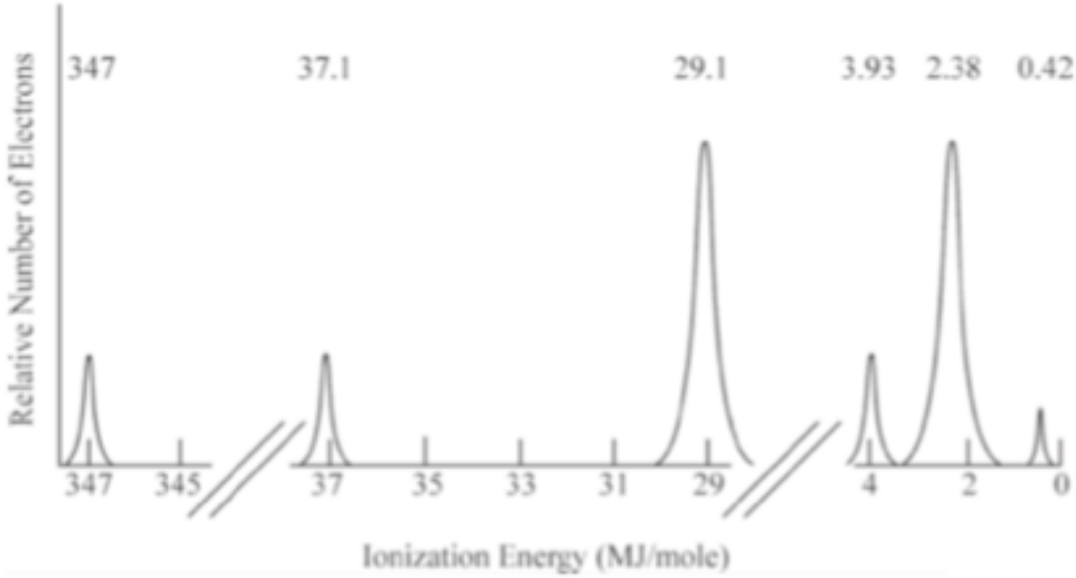


b. Write the electron configuration for this element.

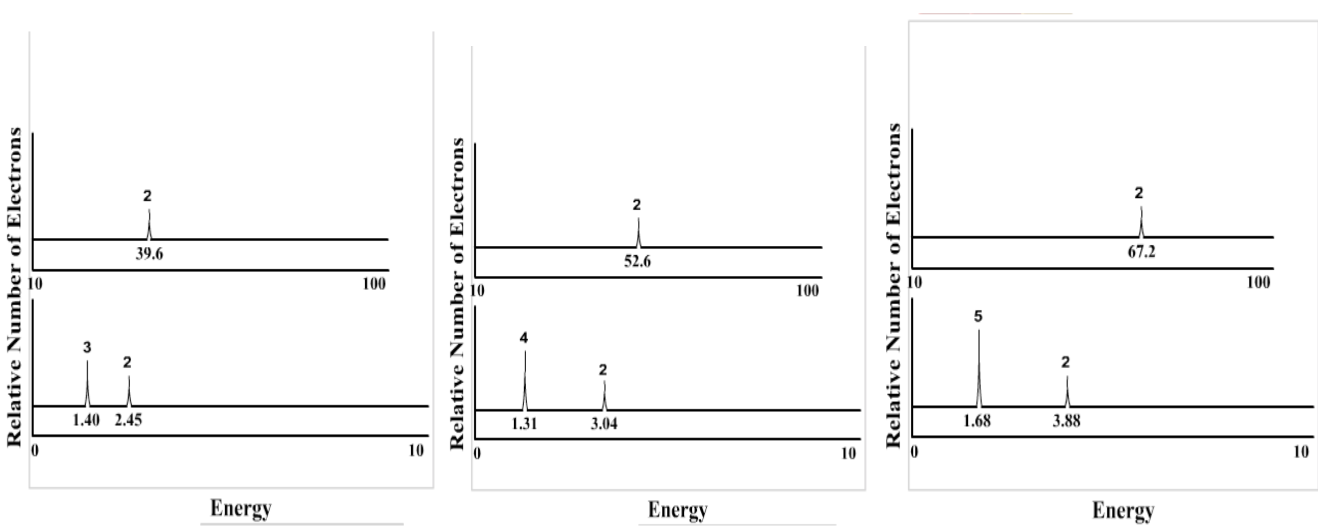
4. Identify if either of the following statements is correct. If yes, why? If not, why not?

a. The photoelectron spectrum of Mg^{2+} is expected to be identical to the photoelectron spectrum of Ne.

b. The photoelectron spectrum of ^{35}Cl is identical to the photoelectron spectrum of ^{37}Cl.



5. For the PES spectrum of potassium above, explain why is the peak at 0.42 MJ/mol identified as being in the 4th energy level.



The spectra above are for nitrogen, oxygen, and fluorine respectively. What is the general trend for ionization energy across a period? When looking at the above spectra, does this trend hold true? Explain why, why not.